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A New Oxidative Degradation of A Bio-recalcitrant α -Carbonyl β -O-4 Lignin Model Compound with Mn(III)/Oxalate System*¹

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Introduction

From environmental viewpoints, microbial and enzymatic delignification have been investigated extensively focusing on the research development of chlorine-free and benign pulp bleaching processes¹⁾. Recently, the biomimetic delignification also has been receiving widespread interests since the first experimental evidence that synthetic and natural iron-porphyrins mimicked the lignin peroxidase (LiP) was reported²⁾. We also reported an example of a manganese peroxidase (MnP)-mimetic system for bleaching kraft pulps as well as for breaking down lignin model compounds³⁾.

We report here a new oxidative system with Mn(III) and oxalate for degradation of a β -O-4 lignin model compound (**1**), which is the poorest substrate of LiP and MnP⁴⁾ and thus bio-recalcitrant. To the extent of our literature survey⁵⁻⁹⁾, neither non-enzymatic nor enzymatic system with Mn(III) have been reported to carry out the cleavage of the substrate (**1**) at room temperature, although similar non-phenolic lignin model compound with the α -carbonyl group has been reported to be degraded in the presence of Fe(III)-octa-carboxyphthalocyanine complex and tert-butylhydroperoxide at room temperature¹⁰⁾, by O₂-alkali treatment to give rise to C $_{\alpha}$ -C $_{\beta}$ bond cleavage products at 100°C¹¹⁾.

Materials and Methods

To a stirred solution of compound (**1**) as substrate (3 μ mol), which had been dissolved in each solvent (DMSO, 1, 4-dioxane or ethanol, 1 ml), 500 μ l of distilled water and 2.7 mg

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(10 μ mol) of Mn(III) acetate were added. The reaction was initiated by the addition of 500 μ l of 100 mM sodium oxalate solution, pH 3.0. The reaction mixtures were incubated at room temperature for 30 minutes, 1 hour, 2 hours and 16 hours under air, 100% N₂ and 100% O₂. The reaction products extracted were subjected to GC-MS, ¹H-NMR and TLC analysis.

Results and Discussion

The substrate (**1**) was found to be broken down with Mn(III) in the presence of oxalate and DMSO under air at room temperature, yielding the C $_{\alpha}$ -C $_{\beta}$ bond cleavage and β -O-4 bond cleavage products such as 4-ethoxyvanillic acid (**2**), vanillin (**3**), 1-(4-ethoxy-3-methoxyphenyl)-2-hydroxy-1-ethanone (**4**) and 4-ethoxy-3-methoxyacetophenone (**5**) (Fig. 1). Almost no reaction occurred in the control system lacking either oxalate, Mn(III) or DMSO. The results show that both of the oxalate and Mn(III) were needed for the reaction. DMSO was the most effective solvent for this reaction system comparison with 1,4-dioxane or ethanol. The yield of the product (**2**) was 14.8% after the reaction with DMSO under air for 16 hours, which was 12 and 25 times those of reactions with 1,4-dioxane and ethanol, respectively.

In order to elucidate the oxygen source for the carboxyl group of the product (**2**) during the C $_{\alpha}$ -C $_{\beta}$ cleavage reaction, the percentage of ¹⁸O-labelled products obtained after the reaction with either ¹⁸O₂, H₂¹⁸O or [¹⁸O]oxalate, were determined. One oxygen atom from O₂ in the atmosphere was incorporated into each of the product (**2**) and the product (**4**) with 43%- and 86%-incorporations, respectively, but not the product (**3**). No oxygen atom was incorporated into the product (**2**) from H₂O under aerobic condition (data not shown). On the other hand, neither H₂O nor oxalate was the oxygen donor for the product (**2**) under anaerobic conditions. The results suggest that the incorporation of oxygen atom from DMSO also occurred under anaerobic condition. Although the reaction mechanisms for

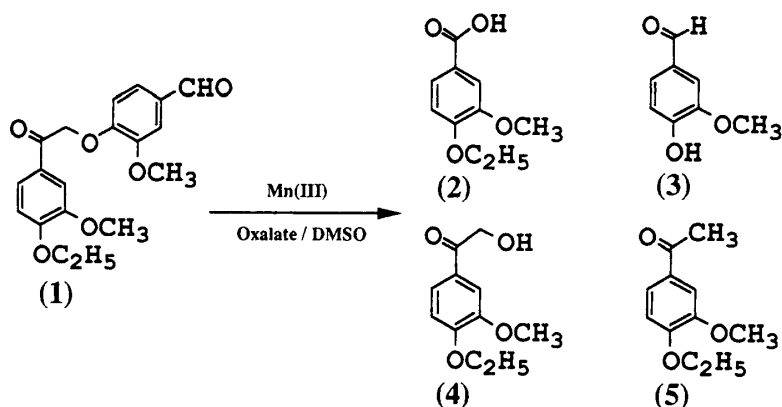


Fig. 1. Substrate (**1**) used and products (**2**–**5**) obtained.

the incorporation of oxygen atom from DMSO is unclear, it is apparent that the reaction mechanism for the degradation of substrate (**1**) was quite different from the one electron oxidation mechanism for lignin peroxidase system, because 1-(4-ethoxy-3-methoxyphenyl)-2-(4-hydroxymethyl-3-methoxyphenoxy)-1-ethanol, which is a good substrate for lignin peroxidase was found not to be broken down in this reaction system by TLC analysis. Furthermore, the nucleophilicity of oxygen atom of DMSO is enough to attack to methyl iodide^{12,13)}. Thus, it is reasonably presumed that the oxygen atom of DMSO attacks the carbonyl moiety of the substrate (**1**) in this system, although the supporting evidence is needed.

In conclusion, the bio-recalcitrant α -carbonyl β -O-4 lignin model compound (**1**) was degraded with Mn(III) in the presence of oxalate and DMSO, yielding the C $_{\alpha}$ -C $_{\beta}$ bond cleavage and the β -O-4 bond cleavage products. The oxygen atom from O₂ in the atmosphere was incorporated into the products (**2**) and (**4**). Dioxygen in the atmosphere, however, is not essential for this reaction system. The mechanisms for the degradation of the substrate (**1**) is quite different from LiP system, but remain to be elucidated.

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